EXHIBIT A

Translation of Japanese Unexamined Patent Application

UREA GREASE COMPOSITION WITH IMPROVED ACOUSTIC PERFORMANCE

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SPECIFICATION

1. Title of the Invention

Urea Grease Composition with Improved Acoustic Performance [2]

2. Claims

1. A grease thickener characterised in that it comprises 90 to 20 mol% of a compound with undernoted general formula (A) and 20 to 90 mol% of a compound with undernoted general formula (B):

(A) $R_1NHCONHR_2NHCONHR_3$

(B) $R_4NHCONHR_5NHCONHR_6$

in which formulas R_2 indicates a bitolylene group, R_1 and R_3 indicate straight-chain or branched saturated or unsaturated alkyl groups with 18 carbons, R_5 indicates a diphenylmethane group, and R_4 and R_6 indicate straight-chain or branched saturated alkyl groups with 8 carbons.

2. A grease thickener characterised in that it comprises 100 parts by weight of a mixture comprising 90 to 20 mol% of a compound with undernoted general formula (A) and 20 to 90 mol% of a compound with undernoted general formula (B); and 5 to 90 parts by weight of a compound with undernoted general formula (C):

(A) $R_1NHCONHR_2NHCONHR_3$

(B) $R_4NHCONHR_5NHCONHR_6$

(C) $R_7NHCONHR_8NHCONHR_9$

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* Numbers in square brackets refer to Translator's Notes appended to the translation.

in which formulas R_2 indicates a bitolylene group, R_1 and R_3 indicate straight-chain or branched saturated or unsaturated alkyl groups with 18 carbons, R_5 indicates a diphenylmethane group, R_4 and R_6 indicate straight-chain or branched saturated alkyl groups with 8 carbons, R_8 indicates a tolylene or bitolylene group, and R_7 and R_9 indicate alkyl-substituted or halogen-substituted aromatic groups.

3. A urea grease composition characterised in that it comprises 2 to 30 parts by weight of the grease thickener of Claim 1 or Claim 2, to 100 parts by weight of mineral oil or synthetic oil.

3. Detailed Description of the Invention

Field of industrial utilisation

The present invention relates to urea grease compositions with improved acoustic performance.

Conventional technology and problems which the invention will solve

Urea greases have come to be used in an extensive range of applications as heat-resistant greases. This is because they generally have higher dropping points and greater thermal stability than greases in which lithium soap is employed as the thickener, and hence can be used for long periods at high temperature. However, although the performance of urea greases is being improved year by year, their track record is still relatively young and for some applications there is much scope for improvement. For example, most commercial urea greases have extremely unsatisfactory acoustic performance and simply cannot be used where such performance is important. For this reason, most greases said to be for low-noise applications are lithium soap based greases. On the other hand, there is a steadily growing demand for smaller, lighter, more precise machinery which is also quieter and capable of giving longer service life. As a matter of course, the bearings that are used in the rotating portions of such machinery are also smaller and end up experiencing higher speeds and increased rotations. Moreover, the greater concentration of components in such machinery means that temperatures are higher, giving rise to very severe conditions as regards the lubrication environment. To cope with these conditions, a great many greases have been studied, but there are hardly any which satisfy all performance aspects. For example, many lithium soap based greases – these being widely used as general-purpose greases – give relatively good acoustic performance and hence most bearings for which acoustic performance is important use a lithium soap based grease. However, lithium soap based greases have lower service temperature limits than heat-resistant greases (such as greases based on urea, clay, complex soaps and sodium terephthalamate) and can hardly be used where high temperatures are encountered. On the other hand, although urea based greases have excellent thermal

stability and are the preferred choice for use in high-temperature locations, their acoustic performance is very poor and they are unsuitable for bearings where acoustic performance is important.

Generally speaking, the mechanism whereby a grease lubricates a bearing is as follows: the grease, which has been packed inside the bearing, is temporarily flung away due to the rotation, after which it undergoes repeated churning and channelling, in the course of which an extremely small quantity of grease or of the oil component is supplied to and lubricates the sliding surfaces. Detected sound originates from vibration produced at these sliding surfaces (between balls or rollers and the race surface or retainer). This vibration may be a vibration of the mechanical bearing itself arising from a dry spot on, or a looseness at, the sliding surfaces; or it may be generated by externally introduced dust or dirt, or by solid foreign matter contained in the grease, getting between the sliding surfaces of the bearing.

Although "solid foreign matter contained in the grease" signifies for example externally introduced dust or dirt, the thickener in the grease is also solid foreign matter, and acoustic performance differs greatly according to the form and type of this thickener. [3]

For example, a lithium soap based grease has a three-dimensional fibrous, gel-like structure obtained by the saponification reaction of lithium hydroxide and a fat or oil, or a fatty acid. The fibres themselves can be soft, or can be made smaller or finer by cooling or other treatment, and hence a grease with good acoustic performance can be produced relatively easily. As another example, a urea grease generally contains, as the thickener, a compound formed by reaction between amines and isocyanates, but many urea compounds obtained by this reaction comprise hard granular particles which are dispersed in an oil to maintain the grease structure. If these granular particles are large, the acoustic performance naturally deteriorates, and therefore acoustic performance is improved to some extent by making these particles finer. Nevertheless, this does not provide a substantial improvement. Some urea greases exhibit good acoustic performance by either maintaining a fibrous structure or by having a thickener comprising soft particles, but these are frequently greases with extremely poor mechanical stability or which soften or harden on exposure to heat.

There are many examples of conventional technology which achieves an improvement in acoustic performance by using an additive such as succinic acid imide or a metallic detergent to obtain a uniform dispersion of the thickener. Such examples are disclosed in Japanese Patent Application Kokai Publication No. 58-018593 ("Diurea Based Grease and Manufacturing Method Thereof"), and in Japanese Patent Application Kokoku Publication No. 62-044039 ("High Dropping Point Lithium Complex Grease Composition"). However,

particularly in the case of urea greases, for the reasons mentioned above the effect of these additives is slight and very little substantial improvement in acoustic performance can be obtained. It is difficult to manufacture a grease with good acoustic performance which also has excellent mechanical stability and heat resistance, and the tendency has been to ignore acoustic performance. An extremely large number of types of urea grease can be produced by varying the kinds of isocyanate and amine used as the raw materials for the thickener, or by varying their combination, and thus the performance of these various types of urea grease is also very diverse. In other words, different urea greases may exhibit completely different characteristics.

Means for solving problems

The present inventors have carried out assiduous research aimed at overcoming the problem of poor acoustic performance that has been encountered with conventional urea grease compositions. This research involved the experimental production of a large number of urea greases. As a result, the inventors have discovered that a grease with truly outstanding acoustic performance and shear stability is obtained by selecting those diurea compounds that resulted in particularly excellent acoustic performance, and mixing these diurea compounds in specific proportions. That is to say, they discovered that a grease containing a thickener obtained by mixing restricted diurea compounds [4] in specific proportions has excellent acoustic performance and shear stability.

Namely, the present invention is a grease thickener characterised in that it comprises 90 to 20 mol% of a compound with undernoted general formula (A) and 20 to 90 mol% of a compound with undernoted general formula (B); and is also a grease thickener characterised in that it comprises 100 parts by weight of a mixture comprising 90 to 20 mol% of a compound with undernoted general formula (A) and 20 to 90 mol% of a compound with undernoted general formula (B), and 5 to 90 parts by weight of a compound with undernoted general formula (C); and is also a urea grease composition characterised in that it comprises 2 to 30 parts by weight of the grease thickener of Claim 1 or Claim 2, to 100 parts by weight of mineral oil or synthetic oil; the general formulas being:

(A) $R_1NHCONHR_2NHCONHR_3$

(B) $R_4NHCONHR_5NHCONHR_6$

(C) $R_7NHCONHR_8NHCONHR_9$

in which formulas R_2 indicates a bitolylene group, R_1 and R_3 indicate straight-chain or branched saturated or unsaturated alkyl groups with 18 carbons, R_5 indicates a diphenylmethane group, R_4 and R_6 indicate straight-chain or branched saturated alkyl groups

with 8 carbons, R_8 indicates a tolylene or bitolylene group, and R_7 and R_9 indicate alkyl-substituted or halogen-substituted aromatic groups.

Preferably, a grease with truly outstanding performance is obtained by ensuring that the content of an above-mentioned thickener is 5 to 20 parts by weight to 100 parts by weight of a mineral oil or synthetic oil. As regards the mixture of diureas (A) and (B), little benefit is obtained from using a mixture if the proportion of compound (B) is less then 20 mol%, and acoustic performance does not improve if the proportion of compound (B) exceeds 90 mol%. Thermal stability is improved and dropping point is increased if 5 to 90 parts by weight of compound (C) are mixed with 100 parts by weight of a mixture of compounds (A) and (B) in which the proportion of compound (B) to compound (A) is 20 to 90 mol%. Little benefit is obtained from using a mixture if the proportion of compound (C) is less than 5 parts by weight, and considerations of consistency yield indicate that it is undesirable for the proportion of compound (C) to exceed 90 parts by weight.

A grease according to the present invention is a diurea grease characterised in that acoustic performance and shear stability are extremely good when (i) a diurea compound in which R_2 is a bitolylene group and R_1 and R_3 are straight-chain or branched saturated or unsaturated alkyl groups with 18 carbons, and a diurea compound in which R_5 is a diphenylmethane group and R_4 and R_6 are straight-chain or branched saturated alkyl groups with 8 carbons, are mixed; or when (ii) a diurea compound in which R_8 is a tolylene or bitolylene group and R_7 and R_9 are alkyl-substituted or halogen-substituted aromatic groups, is added to the above-described mixture. Performance is not benefited at all if diurea compounds are made in which R_1 to R_9 are compounds other than those described above. For example, if R_1 and R_3 are octadecyl groups and R_2 is a diphenylmethane group or a tolylene group, the high-temperature mechanical stability of the diurea grease is markedly poorer. Again, a diurea grease in which the added thickener is typified by R_4 and R_6 having 8 carbons and R_5 being a tolylene or bitolylene group, or a diurea grease in which the added thickener is typified by the alkyl groups having 10 to 14 carbons and R_5 being a tolylene, bitolylene or diphenylmethane group, has poor mechanical stability at high temperatures. Further, a diurea grease in which the added thickener is typified by R_7 and R_9 being alkyl-substituted or halogen-substituted aromatic groups and R_8 being a diphenylmethane group, has very poor acoustic performance.

A grease according to the present invention improves the unsatisfactory acoustic performance and ordinary temperature mechanical stability exhibited when compound (A) is used alone. The invention achieves this by combining, in specific proportions, compound (A), typified by R_1 and R_3 being for example octadecyl groups and R_2 being a bitolylene group,

with compound (B), typified by R_4 and R_6 being for example octyl groups and R_5 being a diphenylmethane group. A grease with an even higher dropping point and even better thermal stability can be obtained – without impairing the performance described above – by further adding compound (C) to the mixture of compounds (A) and (B); compound (C) being typified by R_7 and R_9 being alkyl-substituted or halogen-substituted aromatic groups and R_8 being a tolylene or bitolylene group. Various kinds of additive such as antioxidants, extreme-pressure additives and antiwear agents may be added to further improve the performance of this lubricating grease.

Benefits of the invention

In addition to truly excellent acoustic performance, the diurea grease of the present invention exhibits good thermal and mechanical stability from ordinary to high temperatures. In particular, its grease structure remains stable even after long-term exposure to elevated temperatures, with little tendency to harden or to undergo shear-induced softening. Overall, it is a truly outstanding urea grease which displays, from ordinary to high temperatures, little tendency to soften due to insufficient shear stability. [5]

The substance of the present invention is described below by way of examples.

Examples 1–8

The 3,3′-bitolylene-4,4′-diisocyanate component of compound (A) and 60 wt% of the total quantity of base oil were put in a grease pot in the blending proportions indicated in Table 1, and heated at approximately 80°C. After the diisocyanate had dissolved, the alkylamine component of compound (A) (dissolved in 20 wt% of the total quantity of base oil) was gradually added to the diisocyanate solution and vigorously stirred. After approximately 10 minutes, the diphenylmethane-4,4′-diisocyanate component of compound (B) was added, after which the octylamine component (dissolved in 20 wt% of the total quantity of base oil) was added and stirring continued. The temperature rose due to reaction of the amines with the isocyanates, and after stirring for approximately 30 minutes in this state, the reaction was brought to completion by heating to 170°C. After this, it was left to cool to room temperature, then kneaded to form a grease.

The viscosity of the mineral oil shown in the examples was 11 cSt (at 100°C) and the polyol ester oil had a viscosity of 7 cSt (at 100°C). [6] The results of tests of the consistency, dropping point, Shell roll stability (room temperature and 150°C, 24 hours), consistency after heating at 150°C (measured at 25°C, unworked) and acoustic performance of the grease of each Example are given in Table 1.

Examples 9–21

The diisocyanate and 80 wt% of the total quantity of mineral oil were put in a grease pot in the blending proportions indicated in Table 2, and heated at approximately 80°C. After the diisocyanate was dissolved, the amine (dissolved in 20 wt% of the total quantity of mineral oil) was added and stirred. Stirring was continued for approximately 30 minutes in this state, after which the reaction was brought to completion by heating to 170°C. The solution was left to cool at room temperature, and a grease produced by kneading. Next, greases were produced by mixing the above-described diurea greases formed from compound (C) with the diurea grease of Example 6. The results of tests of the consistency, dropping point, Shell roll stability (room temperature and 150°C, 24 hours), consistency after heating at 150°C (measured at 25°C, unworked) and acoustic performance of the grease of each Example are given in Table 2. A further grease (Example 21) was prepared by incorporating additives such as antioxidants and anti-corrosion agents to the grease of Example 10. The results of tests of this grease are presented in Table 3, in comparison with the results for commercial urea greases.

Measurement methods

Consistency .... JIS K2220

Dropping point .... JIS K2220

Shell roll stability ...... ASTM D1831

Consistency after heating at 150°C........ In conformity with JIS K2220, the grease was packed in a 1/4 consistency measuring apparatus and heated at 150°C for 72 hours. After cooling, the unworked consistency was measured at 25°C.

Acoustic tests .... Measured by the method described in Japanese Patent Application Kokoku Publication No. 53-002357.

Table 1

Example No.			1	2	3	4	5	6	7	8
Compound (A)	3,3′-bitolylene-4,4′-diisocyanate	(g)	7.97	8.09		6.56	4.86	2.73	4.91	4.91
	Stearylamine C18	(g)	16.03			13.22	9.78	5.50		
	Oleylamine C18	(g)		15.91					9.65	9.65
Compound (B)	diphenylmethane-4,4′-diisocyanate	(g)			11.80	2.08	4.60	7.75	4.64	4.64
	Octylamine C8	(g)			12.20	2.14	4.76	8.02	4.80	4.80
Mineral oil		(g)	176	176	176	176	176	176	176	
Polyol ester		(g)								176
Thickener content		(%)	12	12	12	12	12	12	12	12
Compound (A)/Compound (B)		(molar ratio)	100/0	100/0	0/100	75/25	50/50	25/75	50/50	50/50
PROPERTIES										
Consistency (measured at 25°C, worked)			273	276	265	268	269	265	273	284
Dropping point		(°C)	258	195	221	248	252	257	242	245
Shell roll stability after 24 hours	At room temperature		> 440	> 440	283	348	344	333	356	362
	At 150°C		370	344	277	326	315	303	310	331
Consistency after heating at 150°C (25°C, unworked)			148	136	185	157	168	174	163	164
Acoustic test (after 120 seconds)			32	32	51	18	21	23	19	21

Table 2

Example No.		9	10	11	12	13	14	15	16	17	18	19	20
Diurea grease of compound (C)	3,3′-bitolylene-4,4′-diisocyanate (g)	13.25	13.25			12.21	12.21			12.52	12.52		
	2,4/2,6 (65%/35%) tolylene diisocyanate (g)			10.76	10.76			9.74	9.74			10.04	10.04
	para-toluidine (g)	10.75	10.75	13.24	13.24								
	para-chloroaniline (g)					11.79	11.79	14.26	14.26				
	meta-xylidine (g)									11.48	11.48	13.96	13.96
	mineral oil [7] (g)	176	176										
Thickener content (%)		12	12	12	12	12	12	12	12	12	12	12	12
Diurea grease of Ex.6/diurea grease of compound (C) (weight ratio)		0/100	80/20	0/100	80/20	0/100	80/20	0/100	80/20	0/100	80/20	0/100	80/20
PROPERTIES													
Consistency (measured at 25°C, worked)		363	280	372	285	386	287	395	288	346	277	380	286
Dropping point (°C)		>260	>260	>260	>260	>260	>260	>260	>260	>260	>260	>260	>260
Shell roll stability after 24 hours	At room temperature	405	354	>440	358	>440	367	>440	365	>440	369	>440	371
	At 150°C	397	317	>440	327	>440	341	>440	343	>440	336	>440	349
Consistency after heating at 150°C (25°C, unworked)		160	172	181	178	107	159	218	188	53	151	181	180
Acoustic test (after 120 seconds)		157	15	272	20	231	26	642	22	258	25	555	19

Table 3

Test item ↓	Grease →	Example 21	Commercial product A	Commercial product B	Commercial product C
Consistency (measured at 25°C, worked)		284	265	272	281
Dropping point	(°C)	> 260	> 260	242	249
Shell roll stability after 24 hours	At room temperature	362	294	414	343
	At 150°C	327	253	> 440	410
Consistency after heating at 150°C (25°C, unworked)		179	121	148	85
Acoustic test (after 120 seconds)		25	> 10,000	2,020	150

TRANSLATOR'S NOTES

1. Since this application was filed, Nippon Seiko K.K. has changed the English version of the company name to NSK Ltd.

2. I note that there is arguably a discrepancy between the title of the invention and the substance of the claims.

3. This published patent application is followed by an Amendment filed on 9 October 1991 on behalf of the applicants. The Amendment calls for three fairly minor changes to the text of the published application. The first of these changes applies to the present paragraph, and requires that the words "inadequately dispersed" are inserted before the first occurrence of "thickener", thereby changing the single sentence of the paragraph to the following:

   'Although "solid foreign matter contained in the grease" signifies for example externally introduced dust or dirt, inadequately dispersed thickener in the grease is also solid foreign matter, and acoustic performance differs greatly according to the form and type of this thickener.'

4. Sic. The writer presumably means, by "restricted diurea compounds", a restricted set of diurea compounds.

5. Sic. The above-mentioned Amendment calls for a change to this sentence as well. The amended version reads as follows:

   "Overall, it is a truly outstanding urea grease which displays, from ordinary to high temperatures, good shear stability and little tendency to soften."

6. The Japanese text gives "cst" as the abbreviation for the units of viscosity. The writer presumably means to refer to centistokes, so I have corrected the abbreviation to "cSt".

7. The third correction required by the Amendment is to insert the figure "176" for weight of mineral oil in the case of Examples 11 to 20.